

DMFC용 sulfated β -Cyclodextrin/PVA 막

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Synthesis and characterization of poly(vinyl alcohol) membranes containing sulfated β -Cyclodextrin for direct methanol fuel cells

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1. Introduction

Direct methanol fuel cells (DMFC) have attracted considerable attention for several applications because of their lower weight, high efficiency and low poison emissions [1-4]. Perfluorosulfonate ionomer membranes, such as Nafion membranes, are the common membranes used in the polymer electrolyte membrane fuel cells presently. However, applications of Nafion membranes into DMFC are limited by their high cost and poor barrier property to methanol crossover. Therefore it is necessary to develop a proton conductive membrane with low cost and low methanol permeability.

β -Cyclodextrin is a cyclic oligosaccharide consisting of seven glucose units, and the cyclic oligosaccharide has a hydrophobic cavity of several angstroms diameter. It has many reactive sites for the substitution and unique properties forming a formation of rotaxane [5-7].

In this study, we prepared the sulfated β -Cyclodextrin/PVA membranes to reduce the methanol permeability and obtain high proton conductivity through the membrane.

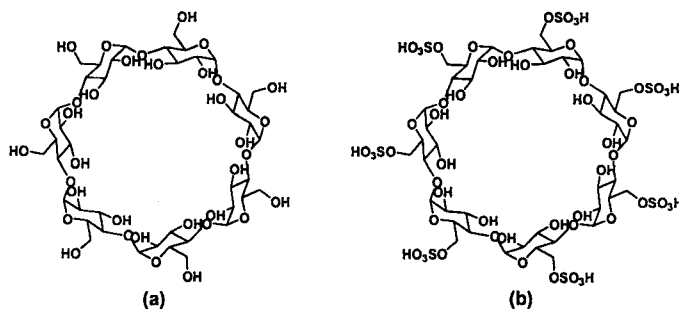


Figure 1. (a) β -Cyclodextrin and (b) sulfated β -Cyclodextrin

2. Experimental

2.1. Materials

PVA (99% hydrolyzed; average Mw = 89,000–98,000; Aldrich), β -Cyclodextrin sulfated sodium salt (Typical substitution 7–11 moles/mole β -CD; Aldrich) Sulfated β -Cyclodextrin was used to prepare ion exchange resins without further purification (Na^+ form \rightarrow H^+ form).

2.2. Membrane preparation

A 5 wt% of PVA solution was mixed with the various amounts of β -CDSO₃H by weight (15%, 25%, 30%, 45%). The mixtures were vigorously stirred at room temperature for 4h. After that, the homogeneous solutions were poured and cast onto a plastic dishes. The membranes were first dried at 25°C for 5 days, dried at 70°C for 2h in a convection oven and cross-linked by a solution of glutaraldehyde (6 g), acetone (300 g) and HCl (8 g) for 3h at 50°C. The membranes were immersed overnight in distilled water to remove impurities.

2.3. Water swelling ratio

The water uptake absorbed in the β -CDSO₃H/PVA membranes was measured by immersing the membrane samples into the distilled water at 25°C for 24h. Then the membranes were taken out, wiped with filter paper, and immediately weighed on a microbalance.

2.4. Proton conductivity measurement

A four-point probe method was used to measure the proton conductivity of the membranes. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water.

2.5. Methanol permeability measurement

The methanol permeability of the membranes was determined using a diffusion cell. This cell consists of two reservoirs, each approximately 48 mL, separated by a vertical membrane. Each membrane is clamped between the two reservoirs and stirred during the experiment.

3. Results and discussion

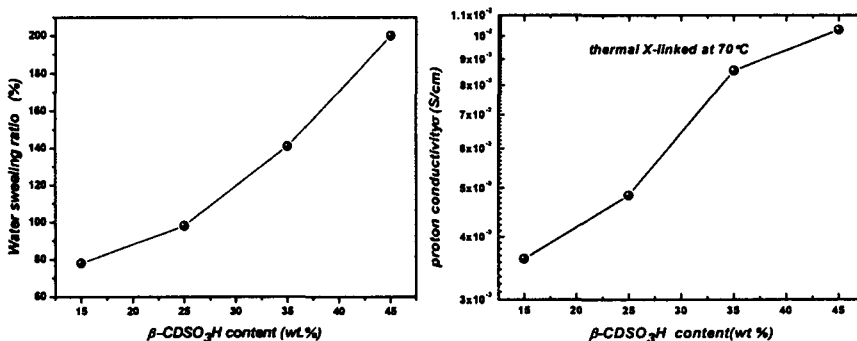


Figure 2. Water swelling ratio (left) and proton conductivity (right) with the concentration of β -CDSO₃H

Fig. 2 shows the water content and proton conductivity in the β -CD SO₃H/PVA membranes depending upon the β -CDSO₃H content added in the case of the membranes prepared at 70°C.

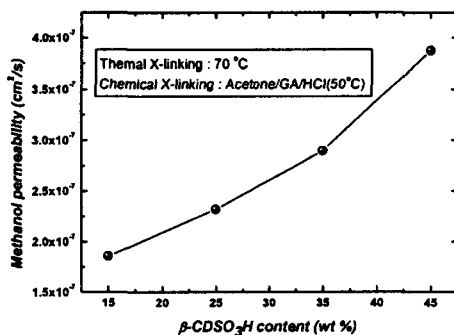


Figure 3. Methanol permeability of PVA/ β -CDSO₃H membranes

Fig. 3 shows the methanol permeability in the β -CDSO₃H/PVA membranes. In the case of the membrane prepared at 70°C, the methanol permeability increased with the amount of the β -CDSO₃H.

4. Acknowledgements

본 연구는 과학기술부 연료전지핵심원천기술개발 (2004-00942)와 창의적 연구 진흥사업 지원으로 수행되었습니다.

5. References

- (1) J. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 4218.
- (2) A. Aramata, I. Toyoshima, M. Enyo, *Electrochim. Acta* 37 (1992) 1317.
- (3) M.P. Hogarth, G.A. Hards, *Platin. Met. Rev.* 40 (4) (1996) 150.
- (4) X. Ren, T.A. Zawadzinski, F. Vribe, H. Dai, S. Gottesfeid, *Electrochem. Soc. proc.* 95 (1995) 284.
- (5) M. I Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, New York, 1978.
- (6) J. L. Atwood, J. E. D. Davies, and D. Macnicole, *Inclusion Compounds*, Academic Press, London, 1984, Vol 13.
- (7) J. Szejtli, *Cyclodextrins and Their Inclusion Complexes*, AKademia Kiado, Budapest, 1982.